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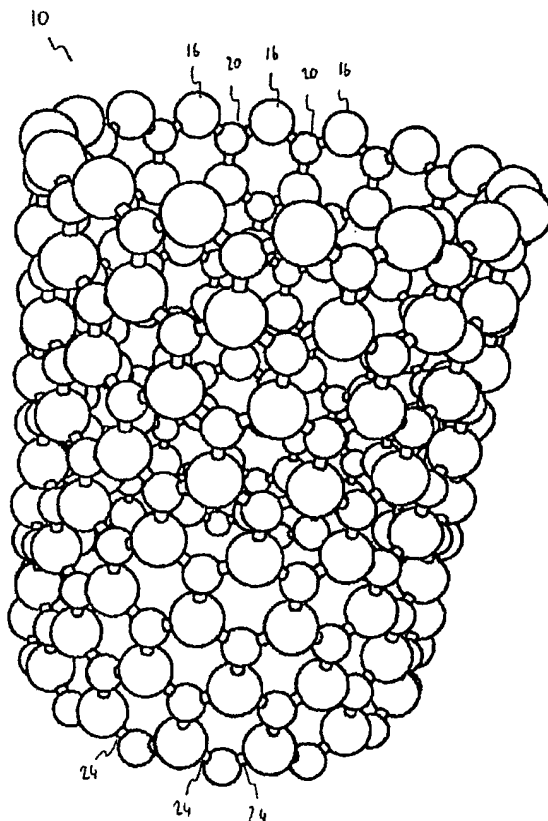
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(54) Title: HYDROGEN STORAGE IN NANOSTRUCTURES WITH PHYSISORTION



(57) Abstract: A hydrogen containing nanostructure is provided, where the hydrogen (28) is adsorbed to the nanostructure by physisorption. The nanostructure includes light elements (16, 20), selected from the second and third rows of the periodic table. The nanostructure is formed as a layered network of light elements coupled with covalent sp² bonds (24). The chemical composition of the nanostructure can be such that the desorption temperature of hydrogen is greater than the liquefaction temperature of nitrogen, 77 K. Further, a hydrogen storage system is provided, including a container and a nanostructured storage material (10) within the container, wherein the nanostructured storage material includes light elements, and the nanostructured storage material is capable of adsorbing hydrogen by physisorption. The hydrogen storage system can include a liquid nitrogen based cooling system, capable of cooling the nanostructured storage material below the desorption temperature of hydrogen. Some embodiments contain a heater to control the temperature of the nanostructured storage material.

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HYDROGEN STORAGE IN NANOSTRUCTURES WITH PHYSISORPTION

BACKGROUND

FIELD OF INVENTION

- 5 The invention relates to hydrogen storage systems, more particularly to the storage of hydrogen in systems that include nanostructures of combinations of light elements.

DESCRIPTION OF RELATED ART

- 10 Hydrogen storage is the key unsolved problem of producing fuel cells for hydrogen-powered automobiles or portable energy devices. In particular, storing hydrogen in large quantities safely and in a light container has proved prohibitively difficult so far.

- Several different techniques have been developed to tackle this problem. In some approaches hydrogen is stored in tanks under high pressure, for example, 300 atm. In other techniques hydrogen is liquefied at temperatures below 20 K with a helium-based cooling system. Both of these techniques pose problems for practical use in automobiles. All of the hydrogen is available for catastrophic release in an accident, raising the risk of explosion or fire. Furthermore, in order to store enough hydrogen to match the range of present day automobiles, the container has to have a volume of at least 50 gallons. Also, both in the high pressure technique and in the helium cooled technique the required containers are heavy, and therefore inefficient for storage. Finally, both techniques also consume a lot of energy for generating the high pressure or for liquefying the hydrogen.

- Some other techniques adsorb hydrogen into solid materials. Several types of materials have been studied in this respect, including metal hydrides and glass microspheres. However, the materials investigated so far all have low hydrogen storage capacity, making them non-competitive with gasoline.

- Hydrogen can be stored in carbon nanostructures, such as graphite and carbon nanofibers, according to the papers of A. Dillon et al. in Nature, vol. 386, p. 377 (1997), A. Chambers et al. in J. Phys. Chem. B vol. 102, p. 3378 (1998), and E. Poirier et al. in Int. J. of Hydrogen Energy, vol. 26, p. 831 (2001), and according to U. S. patent 5,653,951: "Storage of hydrogen in layered nanostructures," by N. Rodriguez and R. Baker; and U. S. patent 4,960,450: "Selection and preparation of activated carbon for

fuel gas storage," by J. Schwarz et al. Furthermore, hydrogen storage in Al and Si containing zeolites and microporous materials has been explored previously.

Nanostructures can be defined as atomic structures that have a spatial extent of less than a few hundred nanometers in one, two, or all three dimensions. A class of
5 nanostructures is formed by planar networks, sometimes referred to as layered compounds. Layered compounds are often formed by elements coupled with sp^2 bonds. The origin of the sp^2 bonds will be presented on the example of elements of the second row of the periodic table, including boron, carbon and nitrogen.

FIG. 1 shows an example of a second row element 4 coupled with sp^2 bonds, or
10 orbitals, 8 to three other elements 12. The s orbital of the second row elements is filled with two electrons, and the p orbitals are partially filled. For example, boron has one electron, carbon has two, and nitrogen has three electrons in the p orbitals. When the second row elements form chemical bonds, one of the s electrons is promoted into an empty p orbital - for example into the p_z orbital in carbon, leaving only one s electron.
15 This one s electron and two of the p electrons first hybridize into three sp^2 hybrid orbitals. The remaining p electrons - none in boron, one in carbon, and two in nitrogen - occupy an orbit that does not participate in the bonding. The three hybridized electrons repel each other, and hence form three sp^2 orbitals 8 as far as possible away from each other. An optimal configuration is when the three sp^2 orbitals 8 make 120
20 degrees with each other, defining a plane. Connecting several second row elements with planar sp^2 orbitals 8 spans the defined plane, thus forming the aforementioned planar networks.

Possible planar networks of the sp^2 bonded materials include triangular lattices. Large sections of a planar network can be deformed to create various nanostructures.

25 Nanostructures that are based on sp^2 bonded triangular lattices include different classes of nanotubes, nanococoons, nanoropes, nanofibers, nanowires, nanohoms, and nanocages.

Storing hydrogen in sp^2 bonded nanostructures has the following advantages. Hydrogen, adsorbed to the nanostructures, desorbs over a range of temperatures, and
30 thus it is not available for catastrophic release, for example, in case of an automobile accident. Furthermore, because of their large surface area, nanostructures are capable

of adsorbing very large quantities of hydrogen, giving rise to a much higher weight % storage efficiency than the aforementioned high pressure and cooling techniques.

However, the above works have the following disadvantages. Typically they considered hydrogen storage at ambient temperatures, where the storage capacity fell far short of the theoretical value, making those works economically non-viable. Also, the works that considered storage at other temperatures reported insufficient storage efficiencies.

In particular, U. S. patent 5,653,951 considered hydrogen storage in carbon nanostructures, utilizing chemisorption. As described below in detail, chemisorption binds hydrogen to the carbon nanostructure by forming a chemical bond that is typically quite strong. Therefore, chemisorptive bonds can change the chemical composition and structure of the storage material itself. This is a drawback for storage applications, as the storage system has to be operated cyclically without structural degradation in order to be useful.

Also, because of the formation of chemical bonds, the hydrogen might be recovered from the storage material in an altered chemical form, for example, methane. This again reduces the usefulness of storage materials, which form chemisorptive bonds.

Therefore, there is a need for hydrogen storage systems that contain sp^2 bonded nanostructures, wherein the chemical composition of the nanostructure is selected to ensure high storage efficiency, the storage system operates at technically advantageous temperatures, and in particular wherein the mechanism of hydrogen adsorption is not chemisorption.

SUMMARY

In accordance with the invention, a hydrogen containing nanostructured storage material is provided, where the hydrogen is adsorbed to the nanostructured storage material by physisorption. The nanostructured storage material includes light elements, belonging to the second and third rows of the periodic table. More specifically, the light elements are selected from Be, B, C, N, O, F, Mg, P, S, and Cl. The chemical composition of the nanostructured storage material is such that the desorption temperature, at which hydrogen desorbs from the nanostructured storage material, is greater than the liquefaction temperature of nitrogen, 77 K. Some

chemical compositions that give rise to a desorption temperature in excess of 77 K are: $B_xC_yN_z$, BN, BC_2N , MgB_2 , Be_3N_2 , BeB_2 , B_2O , B, BeO, $AlCl_3$, Al_4C_3 , AlF_3 , Al_2O_3 , Al_2S_3 , Mg_2Si , Mg_3N_2 , Li_xN_y , Li_xS_y , and Na_xS_y , where x, y, and z are integers.

5 The nanostructured storage material is formed as a layered network of light elements, coupled with covalent sp^2 bonds. The layered network can be a triangular lattice, a nanofiber, a nanoplatelet, a single walled nanotube, a multi walled nanotube, a nanocage, a nanococoon, a nanorope, a nanotorus, a nanocoil, a nanorod, a nanowire, and a fullerene. The layered network can also have a heterogeneous form, including a combination of the above structures, as well as embodiments where various parts of
10 the network can have different chemical composition.

According to another embodiment of the invention, a hydrogen storage system is provided. The hydrogen storage system includes a container and a nanostructured storage material within the container, wherein the nanostructured storage material includes light elements, and the nanostructured storage material is capable of
15 adsorbing hydrogen by physisorption. The nanostructured storage material can be, for example, any of the above-described embodiments. The nanostructured storage material can be combined with a hydrogen distribution system to facilitate the efficient flow of hydrogen.

In some embodiments the hydrogen storage system further includes a cooling system,
20 capable of cooling the nanostructured storage material below the desorption temperature of hydrogen in relation to the nanostructured storage material. In some embodiments the cooling system includes a middle container within the container, separated by vacuum, an inner container within the middle container, and liquid nitrogen between the middle container and the inner container. The nanostructured
25 storage material is within the inner container. Some embodiments contain a heater to control the temperature of the nanostructured storage material.

BRIEF DESCRIPTION OF DRAWINGS

FIG. I illustrates an element with sp^2 bonds.

FIG. 2A illustrates a plan view of a honeycomb nanostructured storage material.

FIG. 2B illustrates a perspective view of a honeycomb nanostructured storage material, displaying the adsorbed hydrogen molecules.

FIG. 3A illustrates a perspective view of a nanotube structure.

FIG. 3B illustrates a perspective view of a nanotube structure, displaying the adsorbed
5 hydrogen molecules.

FIG. 4A illustrates a perspective view of a nanocage structure.

FIG. 4B illustrates a perspective view of a nanocage structure, displaying the adsorbed hydrogen molecules.

FIG. 5 illustrates the sorption and desorption curves of hydrogen in relation to a
10 nanostructured storage material.

FIG. 6 illustrates a cooled hydrogen storage system.

FIG. 7 illustrates the temperature dependence of the hydrogen storage capacity in nanostructured storage materials.

DETAILED DESCRIPTION

15 FIGS. 2A and 2B illustrate an embodiment for storing hydrogen in an sp^2 bonded nanostructured storage material 10 with a triangular lattice that has a flat planar network.

FIG. 2A shows the plan view of nanostructured storage material 10 with a triangular lattice structure, without the hydrogen molecules. The chemical composition of
20 nanostructured storage material 10 is of the AB type, an example of which is boron nitride. Light elements 16 and light elements 20 of nanostructured storage material 10 are shown with bigger and smaller empty circles, respectively. Light elements 16 and 20 are coupled with sp^2 bonds 24. For a discussion of suitable light elements see below.

FIG. 2B shows a perspective view of the triangular lattice, wherein hydrogen
25 molecules 28 are shown in their bonding position. In some embodiments hydrogen molecules 28 are positioned over the center of the hexagons of the triangular lattice, in other embodiments hydrogen molecules 28 are positioned over a bond or over an atom of the lattice. In some embodiments there is one energetically favored position for

hydrogen molecules 28, in other embodiments there are several substantially equivalent positions. In some embodiments the orientation of hydrogen molecules 28 can be parallel to the local plane of the triangular lattice, in other embodiments the orientation can be perpendicular, or it can make some other angle with the local plane of the triangular lattice.

The adsorption properties of hydrogen to nanostructured storage material 10 depend on the nature of sp^2 bonds 24. In some embodiments this property is used, when the adsorption properties of hydrogen to nanostructured storage material 10 are improved by modifying sp^2 bonds 24.

10 Embodiments with modified sp^2 bonds 24 are described, for example, in U.S. patent application entitled: "Increasing Hydrogen Adsorption For Hydrogen Storage In Nanostructured Materials By Modifying sp^2 Covalent Bonds" by Young-Kyun Kwon, Seung-Hoon Jhi, Keith Bradley, Philip G. Collins, Jean-Christophe P. Gabriel, and George Griener.

15 In these embodiments sp^2 bonds 24 are modified, for example, by forming non-planar structures, by introducing various defects, and by introducing different elements into nanostructured storage material 10. In these embodiments the so far passive additional p electron may hybridize to a small degree with the electrons, which formed the sp^2 configuration. Therefore, in these embodiments sp^2 bond 24 may acquire a small sp^3 character. Thus, in these embodiments the covalent bonds of nanostructured storage material 10 may be only substantially sp^2 bonds.

FIGS. A and 3B illustrate some embodiment for storing hydrogen in an sp^2 bonded nanostructured storage material 10 with a planar triangular lattice that has been deformed into a tubular structure, or nanotube.

25 FIG. 3A shows a perspective view of the nanotube without the hydrogen molecules, where the chemical composition of nanostructured storage material 10 is of the AB type, an example of which is boron nitride. Light elements 16 and light elements 20 of nanostructured storage material 10 are shown with bigger and smaller empty circles, respectively. Light elements 16 and 20 are coupled with sp^2 bonds 24.

FIG. 3B shows a perspective view of the nanotube, wherein hydrogen molecules 28 are shown in their bonding position. In some embodiments hydrogen molecules 28 are positioned over the center of the hexagons of the triangular lattice, in other embodiments hydrogen molecules 28 are positioned over a bond or over an atom of the triangular lattice. In some embodiments there is one energetically favored position for hydrogen molecules 28, in other embodiments there are several substantially equivalent positions. In some embodiments the orientation of hydrogen molecules 28 can be parallel to the local plane of the triangular lattice, in other embodiments the orientation can be perpendicular, or it can make some other angle with the local plane of the triangular lattice.

FIGS. 4A and 4B illustrate some embodiment for storing hydrogen in an sp^2 bonded nanostructured storage material 10 with a planar triangular lattice that has been deformed into a cage structure, or nanocage.

FIG. 4A shows a perspective view of the nanocage without the hydrogen, where the chemical composition of nanostructured storage material 10 is of the AB type, an example of which is boron nitride. Light elements 16 and light elements 20 of nanostructured storage material 10 are shown with bigger and smaller empty circles, respectively. Light elements 16 and 20 are coupled with sp^2 bonds 24.

FIG. 4B shows a perspective view of the nanocage, wherein hydrogen molecules 28 are shown in their bonding position. In some embodiments hydrogen molecules 28 are positioned over the center of the hexagons of the triangular lattice, in other embodiments hydrogen molecules 28 are positioned over a bond or over an atom of the triangular lattice. In some embodiments there is one energetically favored position for hydrogen molecules 28, in other embodiments there are several substantially equivalent positions. In some embodiments the orientation of hydrogen molecules 28 can be parallel to the local plane of the triangular lattice, in other embodiments the orientation can be perpendicular, or it can make some other angle with the local plane of the triangular lattice.

In further embodiments hydrogen can be stored in other forms of nanostructured storage material 10. A non-exhaustive list of possible forms of nanostructured storage material 10 includes:

- nanofibers of the following kinds: turbostratic, highly oriented, twisted, straight, curled and rigid;
 - nanotubes of the following kinds: single walled, double walled, multi walled, with zig-zag chirality, or a mixture of chiralities, twisted, straight, bent, kinked, curled, flattened, and round;
 - ropes of nanotubes, twisted nanotubes, braided nanotubes;
 - small bundles of nanotubes (with a number of tubes less than ten), medium bundles of nanotubes (with a number of tubes in the hundreds), large bundles of nanotubes (with a number of tubes in the thousands);
 - nanotorii, nanocoils, nanorods, nanowires, nanohorns;
 - empty nanocages, filled nanocages, multifaceted nanocages, empty nanococoons, filled nanococoons, multifaceted nanococoons;
 - thin nanoplatelets, thick nanoplatelets, intercalated nanoplatelets, with thickness of about 0.3 nm to about 100 nm, and lateral size of about 5 nm to about 500 nm.
- 15 All these structures can assume heterogeneous forms. Heterogeneous forms include structures, where one part of the structure has a certain chemical composition, while another part of the structure has a different chemical composition. An example is a multi walled nanotube, where the chemical composition of the different walls can be different from each other.
- 20 Heterogeneous forms also include different forms of nanostructured storage material 10, where more than one of the above listed forms are joined into a larger irregular structure. Finally, all above d materials can have cracks, dislocations, branches or other imperfections.

It is understood that the scope of the invention extends to all the above listed and described forms of nanostructured storage material 10.

Economic and practical considerations prefer hydrogen storage systems that are light. In particular, light storage systems have higher storage efficiency in the sense that the weight % of the stored hydrogen is higher in light storage systems. Therefore,

embodiments of the present invention include nanostructured storage material 10 composed of light elements. Suitable light elements include elements of the second and third rows of the periodic table: Be, B, C, N, O, F, Mg, P, S, and Cl. The storage efficiency of nanostructured storage material 10 can be enhanced by combining the
5 listed suitable light elements. While Al and Si containing nanostructures, such as zeolites, have been explored before for storage purposes, in some embodiments of the invention Al and Si can be combined with the above light elements.

Some embodiments can contain elements from other rows of the periodic table as well. Some of these elements can be introduced deliberately to enhance a desired property.
10 Other elements may be a residue from the production process, for example, a catalyst. Therefore, it is understood that embodiments of the invention may contain heavier elements in some concentration.

Some embodiments of the invention include $B_xC_yN_z$, where x, y, and z are small integers. Making of this material is described, for example, in "Pyrolytically Grown
15 Arrays of Highly Aligned $B_xC_xN_z$ Nanotubes," by W.-Q. Han, J. Cumings, and A. Zettl in Applied Physics Letters, vol. 78, p. 2769 (2001), and in US patent 6,231,980 "B_xC_yN_z nanotubes and nanoparticles," by M. Cohen and A. Zettl, which publication and patent are hereby incorporated in their entirety by this reference.

Some embodiments of the invention include BN. Making of this material is
20 described, for example, in "Mass Production of Boron Nitride Double-wall Nanotubes and Nanococoons," by J. Cumings and A. Zettl in Chemical Physics Letters, vol. 316, p. 211 (2000), hereby incorporated in its entirety by this reference.

Some embodiments of the invention include BC_2N . Making of this material is described, for example, in "Synthesis of $B_xC_yN_z$ Nanotubules," by Z. Weng-Sieh, K.
25 Cherrey, N.G. Chopra et al., in Physical Review B, vol. 51, p. 11229 (1995), hereby incorporated in its entirety by this reference.

Some embodiments of the invention include MgB_2 . Making of this material is described, for example, in "Superconducting MgB_2 Nanowires," by Y. Wu, B. Messer, and P. Yang in Advanced Materials, vol. 13, p. 1487 (2001), hereby
30 incorporated in its entirety by this reference.

Some embodiments of the invention include Be_3N_2 . Making of this material is described, for example, in "Die Struktur Einer Neuen Modifikation von Be_3N_2 ," by P. Eckerlin and A. Rabenau in *Angewandte Chemie*, vol. 304, p. 218 (1960), hereby incorporated in its entirety by this reference.

- 5 Some embodiments of the invention include BeB_2 . Making of this material is described, for example, in "Absence of Superconductivity in BeB_2 ," by J. Felner in *Physica C*, vol. 353, p. 11 (2001), hereby incorporated in its entirety by this reference.

Some embodiments of the invention include 1320. Making of this material is described, for example, by H. Hall and L. Compton in *Inorganic Chemistry*, vol. 4, p.

- 10 1213 (1965), hereby incorporated in its entirety by this reference.

Some embodiments of the invention include elemental boron. Making of this material is described, for example, by S. La Placa, P. Roland, and J. Wynne in *Chemical Physics Letter* vol. 190, p. 163 (1992), hereby incorporated in its entirety by this reference.

Some embodiments of the invention include standard materials that are listed in the

- 15 Chemical Abstract Service (CAS) at the web site: www.cas.org:

TABLE 1.

Chemical composition	CAS number
BeO	1304-56-9
AlCl_3	7784-13-6
Al_4C_3	1299-86-1
AlF_3	7784-18-1
Al_2O_3	1344-28-1
Al_2S_3	1302-81-4
Mg_2Si	22831-39-6
Mg_3N_2	12057-71-5
Li_3N	26134-62-3
Li_2S	12136-58-2
Na_2S	1313-82-2
Na_2S_4	12034-39-8

In the above embodiments of the invention the hydrogen atoms bond to nanostructured storage material 10 by physisorption. Therefore, the present invention differs from U.S. patent 5,653,951, which describes an invention, where "... nanostructures of the present invention store hydrogen by chemisorbing molecular hydrogen in the interstices of the nanostructure" (col. 3, ll. 40-42).

There are several crucial differences between physisorption and chemisorption. The following comparative table is assembled according to the Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons, (2001):

TABLE 2.

Parameter I	Physisorption	Chemisorption
interaction of adsorption	no electron transfer, adsorption by physical interactions	electron transfer, leading to the formation of a chemical bond between adsorbate and surface
activation energy	small, often immeasurable	considerable
desorption	rapid, non-activated	slow, activated

10

As Table 2 states, chemisorption is a type of adsorption, where an adsorbate is bound to a surface by the transfer of electrons, forming a chemical bond between the adsorbate and atoms of the surface. In contrast, physisorption is a type of adsorption, where an adsorbate is bound to a surface by physical interactions without the transfer of electrons.

Physical interactions, giving rise to physisorption, include, but are not restricted to, Van der Waals interactions. Van der Waals interactions are operational when the neutral atoms or molecules of the adsorbate and the surface polarize each other, and the polarized atoms or molecules attract each other at some distance.

Accordingly, chemisorptive bonds are strong and physisorptive bonds are weak. This difference manifests itself in the kinetics of the dissolution of the bonds, or desorption. Chemisorptive bonds are dissolved by an activated process, i.e., by thermal activation over an activation energy barrier, which is considerable. For this reason dissolution of chemisorbed bonds proceeds slowly and is not adiabatically reversible.

In contrast, physisorptive bonds are dissolved by a non-activated process. The activation energy is small, in many cases immeasurably small. Hence physisorptive bonds dissolve rapidly and reversibly.

U.S. Patent 5,653,951 discusses in great detail the irreversible aspects of desorption of that invention. The irreversibility of desorption of that invention is illustrated in FIGS. 5
IA, 1 B, 2B, 3A, and 3B by the fact that the sorption and desorption curves do not coincide. Such irreversibility is strong evidence for the chemisorptive nature of hydrogen bonding in U.S. Patent 5,653,951.

FIG. 5 illustrates the coverage fraction, i.e., the fraction of the adsorbent surface, which
is covered by hydrogen, as a function of pressure at a fixed temperature. The solid sorption curve indicates the results for starting at a low pressure value, for example, 10^{-3} atm, and measuring the coverage fraction while increasing the pressure. The dashed desorption curve indicates the results for starting at a high pressure value, for example, 1 atm, and measuring the coverage fraction while decreasing the pressure.

In contrast to U.S. Patent 5,653,951, as shown in FIG. 5, the sorption and desorption curves of the present invention substantially coincide, indicating that the adsorption occurs by physisorption.

The above embodiments can be manufactured by different techniques. The two main acts of manufacturing are the making of nanostructured storage material 10 and the subsequent purifying of nanostructured storage material 10.

According to some methods of the invention, the making of nanostructured storage material 10 starts by providing the bulk material with the desired chemical composition in polycrystalline or micrograined form. The bulk material is then loaded into a ball mill. The balls of the ball mill can be stainless steel balls or hard ceramic balls, with a
diameter of, for example, about 3 mm. The material can be milled for an extended period, for example, 24 hours. The milling can take place in air, in vacuum, or in reactive gases. The resulting material will contain some nanostructured storage material 10, which can be separated by subsequent purifying.

According to some other methods of the invention, the making of nanostructured storage material 10 starts with providing a bulk material in powder form. In some

embodiments the bulk material has the desired chemical composition, in others the bulk material contains some of the desired ingredients. The powdered bulk material is pressed into a shape, suitable for functioning as an electrode, an example of such a shape being a rod. The rod is then used as an electrode to construct an arc chamber.

- 5 The construction of such an arc chamber is described, for example, in "A Mass Production of Boron Nitride Double Wall Nanotubes and Nanocacoons," by J. Cumings and A. Zettl in Chemical Physics Letters, vol. 316, p. 211 (2000). The arc chamber can be filled up with inert gases, for example, helium. In some embodiments the arc chamber can be filled up by one or more reactive gas. For example, beryllium nitride, 10 Be₃N₂, could be made in an arc chamber whose electrode contains beryllium and where the chamber contains nitrogen gas.

- Subsequent purifying of nanostructured storage material 10 can be performed by many methods. Some purifying methods are described by A. Dillon et al. in Advanced Materials, vol. 11, p. 1354 (1999), G. Duesberg et al. in Applied Physics A, vol. 67, p. 117 (1998), K. Shelimov et al. in Chemical Physics Letters, vol. 282, p. 429 (1998), J. 15 Tak et al. in Chemical Physics Letters, vol. 344, p. 18 (2001), P. Young et al. in Carbon, vol. 39, p. 655 (2001), which publications are hereby incorporated in their entirety by this reference. Purifying methods are capable of extracting nanostructured storage material 10 of a particular class and form, for example, corresponding to the above list 20 of nanostructured storage materials 10.

- FIG. 6 illustrates an embodiment of a hydrogen storage system 100 according to the invention. An outer container 104 contains vacuum in outer region 108 to insulate the internal parts of hydrogen storage system 100 from the heat of the environment. The vacuum in outer region 108 can be controlled through vacuum valve 110. A pump can 25 be coupled to vacuum valve 110 to reduce the pressure in outer region 108. In some embodiments the pressure in outer region 108 is between about 10^9 atm and 10^{-1} atm, for example, 10^{-6} atm.

Middle container 112 contains a cooling substance 116 to provide cooling of hydrogen storage system 100. Cooling substance 116 can be, for example, liquid nitrogen.

- 30 Cooling systems utilizing liquid nitrogen have multiple advantages over systems utilizing liquid helium. Liquid nitrogen is much cheaper per liter than liquid helium.

Nitrogen becomes a liquid at 77 K, whereas helium becomes a liquid at 4.2 K. It requires much less energy to cool a system to a temperature of 77 K, than to a temperature of 4.2 K. It also requires a much simpler, and therefore lighter cooling apparatus to maintain a temperature of 77 K, than to maintain a temperature of 4.2 K.

5 Cooling valve 114 is used to control the cooling substance. For example, cooling substance 116 can be supplied through cooling valve 114, and the evaporated excess cooling substance 116 can be released through cooling valve 114. In embodiments that use different hydrogen storage materials other cooling substances 116 may be utilized.

10 Inner container 120 contains nanostructured storage material 10. Nanostructured storage material 10 can be any embodiment described above or a combination thereof. In some embodiments nanostructured storage material 10 substantially fills up inner container 120. In other embodiments nanostructured storage material 10 is combined with a hydrogen distribution system, which provides paths for the hydrogen to flow
15 efficiently across the volume of nanostructured storage material 10. The hydrogen distribution system can be, for example, a hierarchical network of tubes of varying diameters to facilitate the efficient flow of hydrogen.

A hydrogen valve 126 is used to control the hydrogen gas. Hydrogen storage system 100 can be filled by coupling hydrogen valve 126 to a hydrogen container through a
20 pump.

FIG. 7 illustrates the hydrogen storage capacity in percents in nanostructured storage material 10 as a function of the temperature. The amount of stored hydrogen is normalized with the amount stored at zero temperature. The curves refer to pressures of 1 atm, 10 atm, and 100 atm. FIG. 7 illustrates that as the temperature is increased
25 from a low value, hydrogen starts the desorption at a relatively well defined desorption temperature T_D . The value of T_D depends on the pressure, as shown. When the temperature is raised to about 120% of T_D at 1 atm, and to about 150% of T_D at 100atm, substantially all hydrogen is released. The value of T_D is about 60 K for carbon nanostructures and higher for boron nitride nanostructures. In FIG. 7 the
30 temperature is given relative to the desorption temperature T_D at 1 atm, $T_D(1 \text{ atm})$.

The amount of hydrogen adsorbed in a storage material can be characterized by the percentage wise weight increase of the storage system caused by the adsorption of hydrogen, in units of weight %.

Several papers addressed the storage of hydrogen in nanostructures at ambient
5 temperatures. For most nanostructured materials the desorption temperature is well below ambient temperature, in accordance with the fact that physisorptive bonds are weak. Therefore, the amount of hydrogen stored in these nanostructures at ambient temperature is rather small.

For example, M. Ashraf Imam and R. Loufty report in "Hydrogen Adsorption of
10 Different Types of Nanotubes," on p. 40 of the Proceedings of NT'01, the International Workshop of on the Science and Applications of Nanotubes, hereby incorporated in its entirety by this reference, that single walled nanotubes adsorb hydrogen in an amount between about 0. 30 weight % and about 0. 50 weight %.

In contrast, embodiments of the invention store hydrogen in cooled storage systems at
15 temperatures below the desorption temperature, enabling the storage of much larger quantities. In the above units hydrogen adsorption below the desorption temperature in some embodiments is between about 3 weight % and about 27 weight %, for example, 7.5 weight %. Operating hydrogen storage system 100 below the desorption temperature enhances the storage capacity by a factor of 30 or more in comparison to
20 operating the hydrogen storage system 100 at ambient temperatures.

At the same time embodiments of the invention are operated at or above liquid nitrogen temperatures, and thus do not require the use of liquid helium for cooling purposes. As discussed above, cooling systems using liquid nitrogen have many advantages over cooling systems using liquid helium.

25 Storage systems that advantageously use liquid nitrogen as cooling substance 116 require nanostructured storage materials 124 that have a desorption temperature above 77 K. The desorption temperature of nanostructured storage material 10 depends on its chemical composition. In particular, while pure carbon nanostructures typically have desorption temperatures below 77 K, embodiments that use nanostructured
30 storage materials 124 formed from a combination of light elements have desorption

temperatures well above 77 K. For example, boron nitride has a desorption temperature which is about 30% higher than that of carbon.

Storage systems with higher desorption temperatures require less energy for their operation. In particular, storage systems with desorption temperatures at or above the ambient temperature do not require a cooling system, making the storage system much lighter. Suitable selection of the chemical composition of nanostructured storage material 10 may increase the desorption temperature to ambient temperature.

The operation of hydrogen storage system 100 includes filling up the system with hydrogen and recovering stored hydrogen from the system.

Hydrogen storage system 100 can be filled up by coupling hydrogen valve 126 to a hydrogen container through a pump. Nanostructured storage material 10 is cooled by cooling substance 116 to temperatures below the desorption temperature. When the pressure of the pump is raised to a suitable value, hydrogen from the hydrogen container will be pumped into inner container 120, where it will adsorb to nanostructured storage material 10. Suitable pressure values can lie in the range of, for example, about 1 atm to about 20atm.

Hydrogen can be recovered from hydrogen storage system 100 by various methods. Some embodiments recover the hydrogen by heating nanostructured storage material 10 with heater 130. Heater 130 can be, for example, a resistor, driven by a current.

The longer the current is applied to heater 130, or the more current is applied to heater 130, the higher the temperature of nanostructured storage material 10 will rise. As the temperature rises above the desorption temperature, hydrogen will desorb from nanostructured storage material 10, and can be recovered through hydrogen valve 126. In some other embodiments simply the leakage heat, leaking into inner container 120 from the outside, can be used to drive the desorption of hydrogen.

[0084] Although the various aspects of the present invention have been described with respect to certain embodiments, it is understood that the invention is entitled to protection within the full scope of the appended claims.

CLAIMS

We claim:

1. A hydrogen storage nanostructure, comprising:
 5 a nanostructured storage material, comprising
 a plurality of light elements, wherein the light elements are
 selected from
 the group consisting of Be, B, C, N, O, F, Mg, P, S, and Cl; wherein
 the nanostructured storage material is adapted to absorb
 10 hydrogen by physisorption.
2. The hydrogen storage nanostructure of claim 1, wherein
 the nanostructured storage material is adapted to absorb hydrogen
 without the formation of a chemical bond.
3. The hydrogen storage nanostructure of claim 1, wherein
 15 the nanostructured storage material is adapted to adsorb hydrogen with
 van der Waals interactions.
4. The hydrogen storage nanostructure of claim 1, wherein
 the chemical composition of the nanostructured storage material is
 selected from
 20 the group consisting of $B_xC_yN_z$, BN, BC_2N , MgB_2 , Be_3N_2 , BeB_2 , B_2O , B,
 BeO , $AlCl_3$, Al_4C_3 , AlF_3 , Al_2O_3 , Al_2S_3 , Mg_2Si , Mg_3N_2 , Li_3N , Li_2S , Na_2S , and Na_2S_4 ,
 wherein
 the nanostructured storage material has a chemical composition; and
 x, y, and z are integers.
- 25 5. The hydrogen storage nanostructure of claim 4, wherein
 the chemical composition of the nanostructured storage material is
 such that the desorption temperature of hydrogen in relation to the
 nanostructured storage material is
 greater than the liquefaction temperature of nitrogen, wherein the hydrogen has
 30 a desorption temperature in relation to the nanostructured storage material.
6. The hydrogen storage nanostructure of claim 1, wherein the
 nanostructured storage material comprises:

a network of the plurality of light elements coupled with covalent bonds.

7. The hydrogen storage nanostructure of claim 6, wherein the covalent bonds comprise:

substantially sp^2 bonds.

5 8. The hydrogen storage nanostructure of claim 1, wherein the nanostructured storage material comprises:

a layered network of the plurality of light elements.

9. The hydrogen storage nanostructure of claim 1, wherein the nanostructured storage material comprises:

10 at least one of a triangular lattice, a nanofiber, a nanoplatelet, a single walled

nanotube, a multi walled nanotube, a nanocage, a nanococoon, a nanohorn, a nanorope,

a nanotorus, a nanocoil, a nanorod, a nanowire, and a fullerene.

15 10. The hydrogen storage nanostructure of claim 9, wherein the at least one of a triangular lattice, a nanofiber, a nanoplatelet, a single walled

nanotube, a multi walled nanotube, a nanocage, a nanococoon, a nanohorn, a nanorope,

20 a nanotorus, a nanocoil, a nanorod, a nanowire, and a fullerene-like molecule is in a

heterogeneous form.

11. A hydrogen storage nanostructure, comprising:

a nanostructured storage material, comprising:

25 at least one light element, wherein the at least one light element is selected from the group consisting of Be, B, N, P, and S, wherein

hydrogen, adsorbed to the nanostructured storage material adapted to absorb hydrogen by physisorption.

12. A hydrogen storage system, comprising:

30 a container; and

a nanostructured storage material, disposed within the container,

wherein

the nanostructured storage material comprises a plurality of

light

elements, wherein the light elements are selected from the group consisting of

Be, B, C, N; O, F, Mg, P, S, and Cl; and

the nanostructured storage material is adapted to adsorb hydrogen by physisorption.

13. The hydrogen storage system of claim 12, wherein the nanostructured storage material is capable of adsorbing hydrogen without the formation of a chemical bond.

14. The hydrogen storage system of claim 12, wherein the nanostructured storage material is adapted to adsorb hydrogen by van der Waals interactions.

15. The hydrogen storage system of claim 12, wherein the chemical composition of the nanostructured storage material is selected from

the group consisting of $B_xC_yN_z$, BN, BC_2N , MgB_2 , Be_3N_2 , BeB_2 , B_2O , B, BeO, $AlCl_3$,

Al_4C_3 , AlF_3 , Al_2O_3 , Al_2S_3 , Mg_2Si , Mg_3N_2 , Li_3N , Li_2S , Na_2S , and Na_2S_4 , wherein

the nanostructured storage material has a chemical composition; and x, y, and z are integers.

16. The hydrogen storage system of claim 15, wherein the chemical composition of the nanostructured storage material is such that the

desorption temperature of hydrogen in relation to the nanostructured storage material is

greater than the liquefaction temperature of nitrogen, wherein hydrogen has a desorption

temperature in relation to the nanostructured storage material.

17. The hydrogen storage system of claim 12, wherein the nanostructured storage material comprises:

a network of the plurality of light elements coupled with covalent bonds.

18. The hydrogen storage system of claim 17, wherein the covalent bonds comprise: substantially sp^2 bonds.

19. The hydrogen storage system of claim 12, wherein the nanostructured storage material comprises:
a layered network of the plurality of light elements.
20. The hydrogen storage system of claim 19, wherein the layered network
5 comprises:
at least one of a triangular lattice, a nanofiber, a nanoplatelet, a single walled
nanotube, a multi walled nanotube, a nanocage, a nanococoon, a nanoborn, a nanorope,
10 a nanotorus, a nanocoil, a nanorod, a nanowire, and a fullerene.
21. The hydrogen storage system of claim 20, wherein
the at least one of a triangular lattice, a nanofiber, a nanoplatelet, a single walled nanotube, a multi walled nanotube, a nanocage, a nanococoon, a nanohorn, a nanorope, a nanotorus, a nanocoil, a nanorod, a nanowire, and a fullerene-like molecule
15 is in heterogeneous form.
22. The hydrogen storage system of claim 12, wherein the nanostructured storage material is combined with a hydrogen distribution system within the container.
23. The hydrogen storage system of claim 12, further comprising:
20 a cooling system, capable of cooling the nanostructured storage material below the desorption temperature of hydrogen in relation to the nanostructured storage material.
24. The hydrogen storage system of claim 23, wherein the cooling system
25 comprises:
a middle container, disposed within the container;
a heat insulator, disposed between the container and the middle container, capable of reducing the exchange of heat between the container and the middle container;
30 an inner container, disposed within the middle container; and
a cooling substance, disposed between the middle container and the inner
container, capable of reducing the temperature of the inner container.
25. The hydrogen storage system of claim 24, wherein

the heat insulator is a gaseous substance, having a pressure less than 10^{-1} atm.

26. The hydrogen storage system of claim 24, wherein the cooling substance is liquid nitrogen.
- 5 27. The hydrogen storage system of claim 24, further comprising: a heat insulating valve, coupled to the container, capable of controlling the heat insulator; a cooling valve, coupled to the middle container, capable of controlling the cooling substance; and
- 10 a hydrogen valve, coupled to the inner container, capable of controlling the hydrogen.
28. The hydrogen storage system of 24, further comprising: a heater, disposed within the inner container, capable of controlling the temperature of the nanostructured storage material.
- 15 29. The hydrogen storage system of claim 24, further comprising: a fuel cell, wherein the hydrogen recovered from the hydrogen storage system is used in the fuel cell to generate energy.
30. A hydrogen storage system, comprising:
 - 20 container means; and nanostructured storage means, disposed within the container means, wherein the nanostructured storage means comprises a plurality of light elements, wherein the light elements are selected from the group consisting of Be, B, C, N,
 - 25 O, F, Mg, P, S, and Cl; and the nanostructured storage means is adapted to adsorb hydrogen by physisorption.
 31. A hydrogen storage system, comprising: a container; and
 - 30 a nanostructured storage material, disposed in the container, wherein the nanostructured storage material comprises at least one light element, wherein the at least one light element is selected from the group consisting

of Be, B, N, P, and S; and
the nanostructured storage material is adapted to adsorb
hydrogen by physisorption.

32. A hydrogen storage nanostructure, comprising:
5 a nanostructured storage material, comprising a plurality of light
elements,
wherein the light elements are selected from the group consisting of Be, B, C,
N, O, F, Mg, Al, Si, P, S, and Cl, wherein
the nanostructured storage material is not a microporous material

10 or

zeolite, wherein
the nanostructured storage material is adapted to adsorb
hydrogen by physisorption.

33. A method of storing hydrogen, the method comprising:
15 providing a nanostructured storage material in a container, the
nanostructured storage material comprising:
a plurality of light elements, wherein the light elements are
selected from the group consisting of Be, B, C, N, O, F, Mg, P, S, and Cl; and
introducing hydrogen into the nanostructured storage material,

20 wherein

the hydrogen adsorbs to the nanostructured storage material by
physisorption.

34. The method of claim 33, wherein providing the nanostructured storage
material comprises:

25 selecting the chemical composition of the nanostructured storage
material so that

the desorption temperature of hydrogen in relation to the nanostructured storage
material

30 is greater than the liquefaction temperature of nitrogen, wherein hydrogen has a
desorption temperature in relation to the nanostructured storage material, and
wherein

the nanostructured storage material has a chemical composition.

35. The method of claim 33, wherein providing the nanostructured storage
material comprises:

providing the nanostructured storage material in combination with a hydrogen

distribution system within an inner container.

36. The method of claim 33, further comprising:

5 cooling the nanostructured storage material below the desorption temperature of

the hydrogen in relation to the nanostructured storage material.

37. The method of claim 36, wherein cooling the nanostructured storage material comprises:

10 providing a middle container, disposed within the container;

providing a heat insulator, disposed between the container and the

middle

container, capable of reducing the exchange of heat between the container and the

15 middle container;

providing an inner container, disposed within the middle container; and

providing a cooling substance, disposed between the middle container

and the

inner container, capable of reducing the temperature of the inner container.

20 38. The method of claim 37, wherein providing the cooling substance comprises:

providing liquid nitrogen, as a cooling substance.

39. The method of claim 37, further comprising:

controlling the heat insulator with a heat insulating valve, coupled to the

25 container;

controlling the cooling substance with a cooling valve, coupled to the

middle

container; and

controlling the hydrogen with a hydrogen valve, coupled to the inner

30 container.

40. The method of claim 37, further comprising:
controlling the temperature of the nanostructured material with a
heater,
disposed within the inner container.

5

3

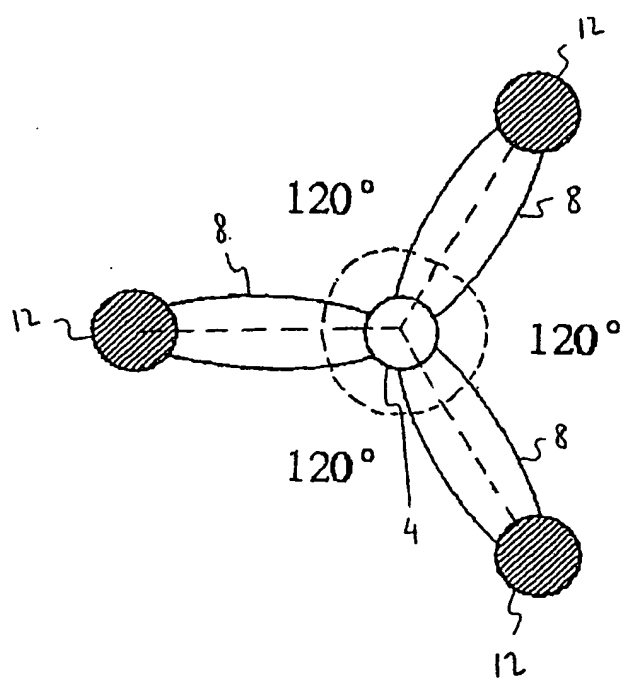


Figure 1

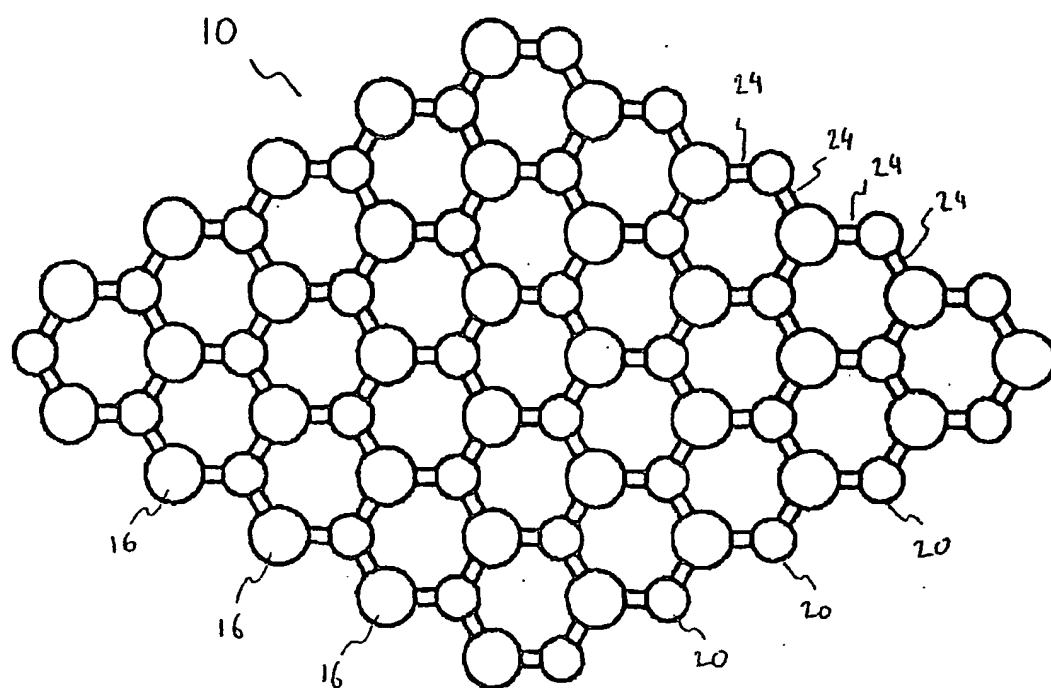


Figure 2

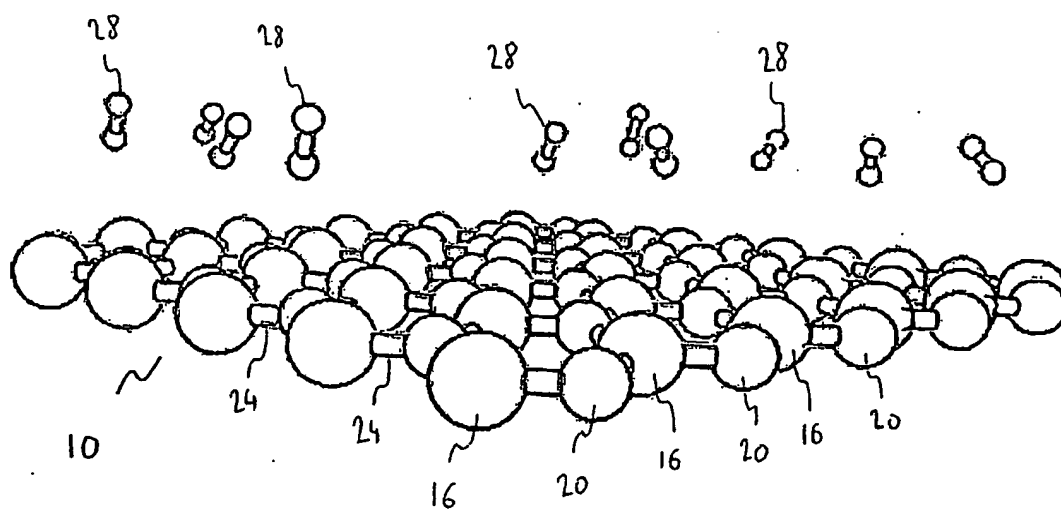


Figure 3

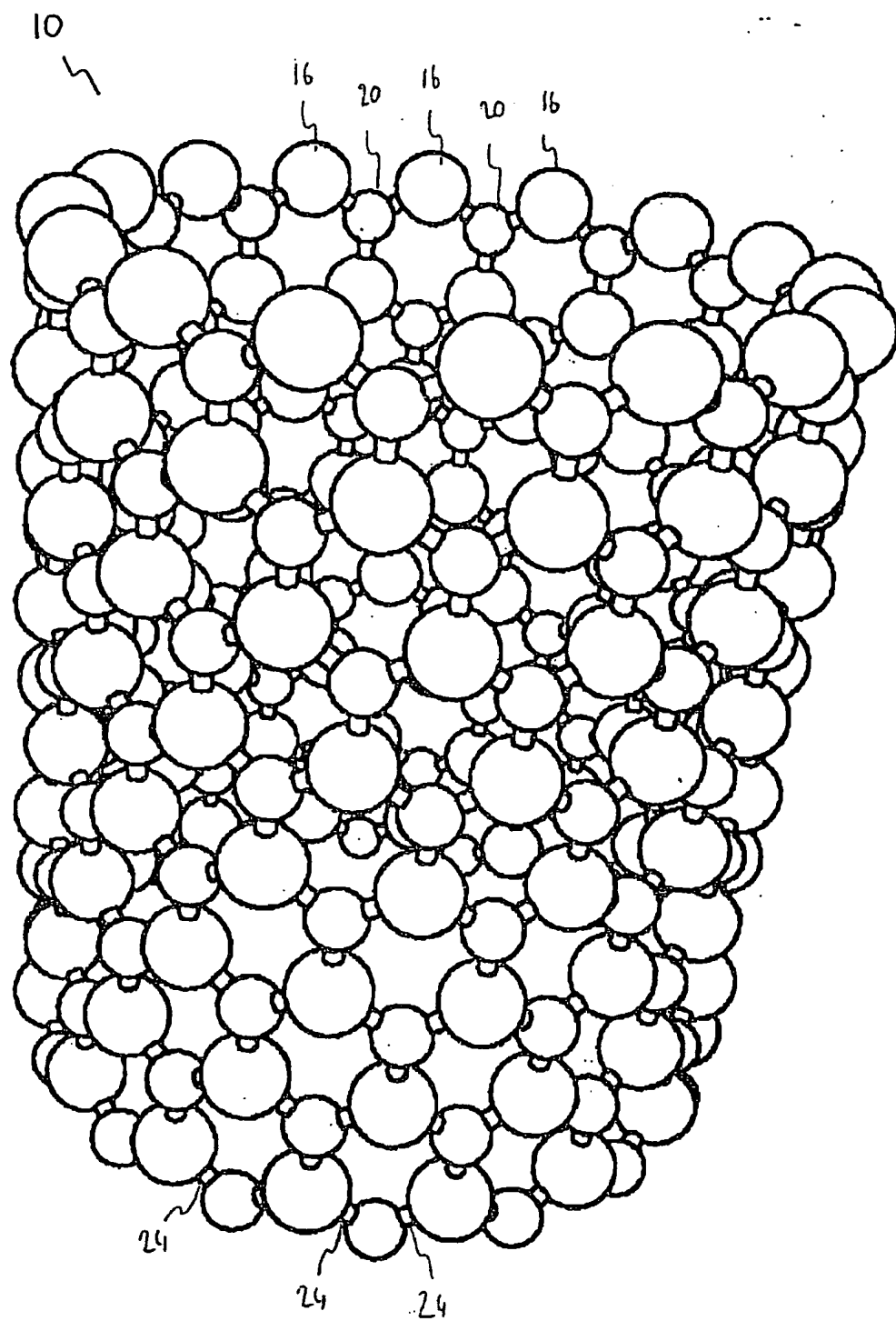


Figure 4

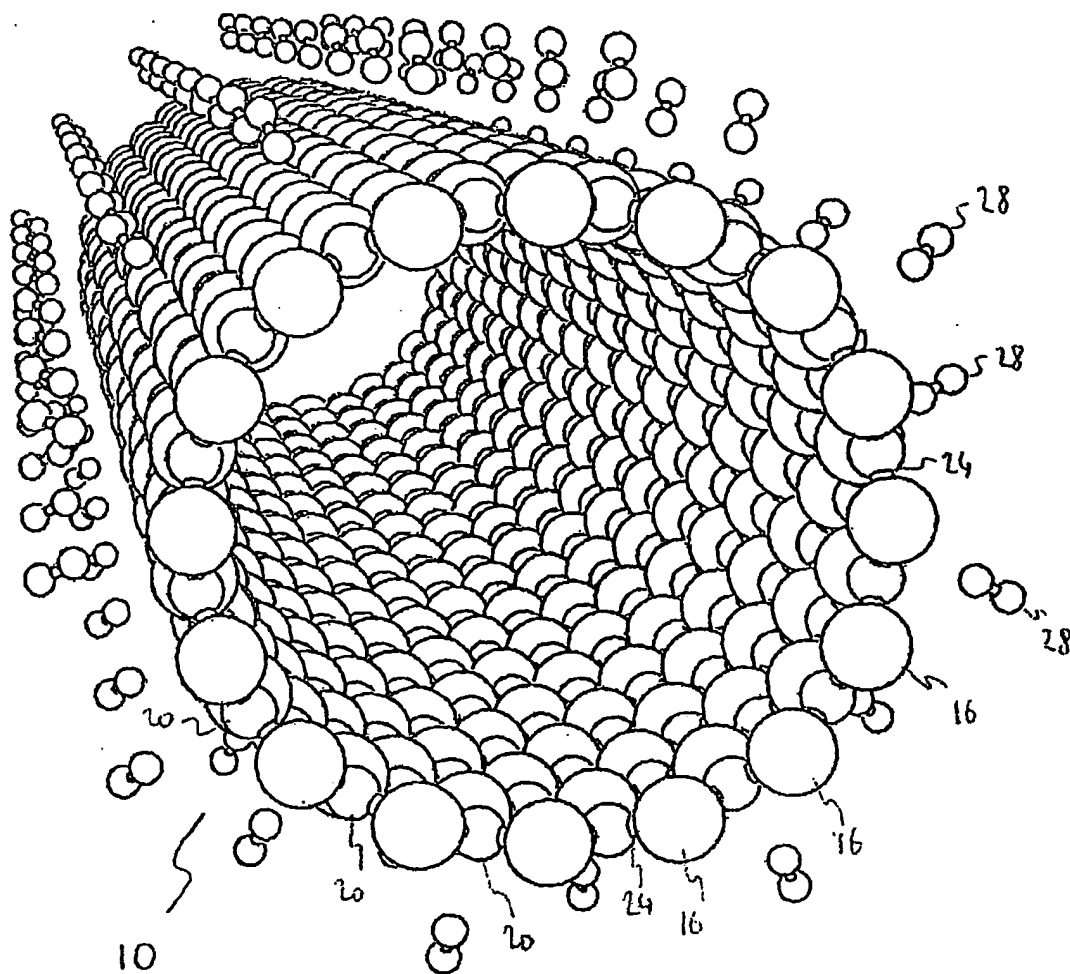


Figure 5

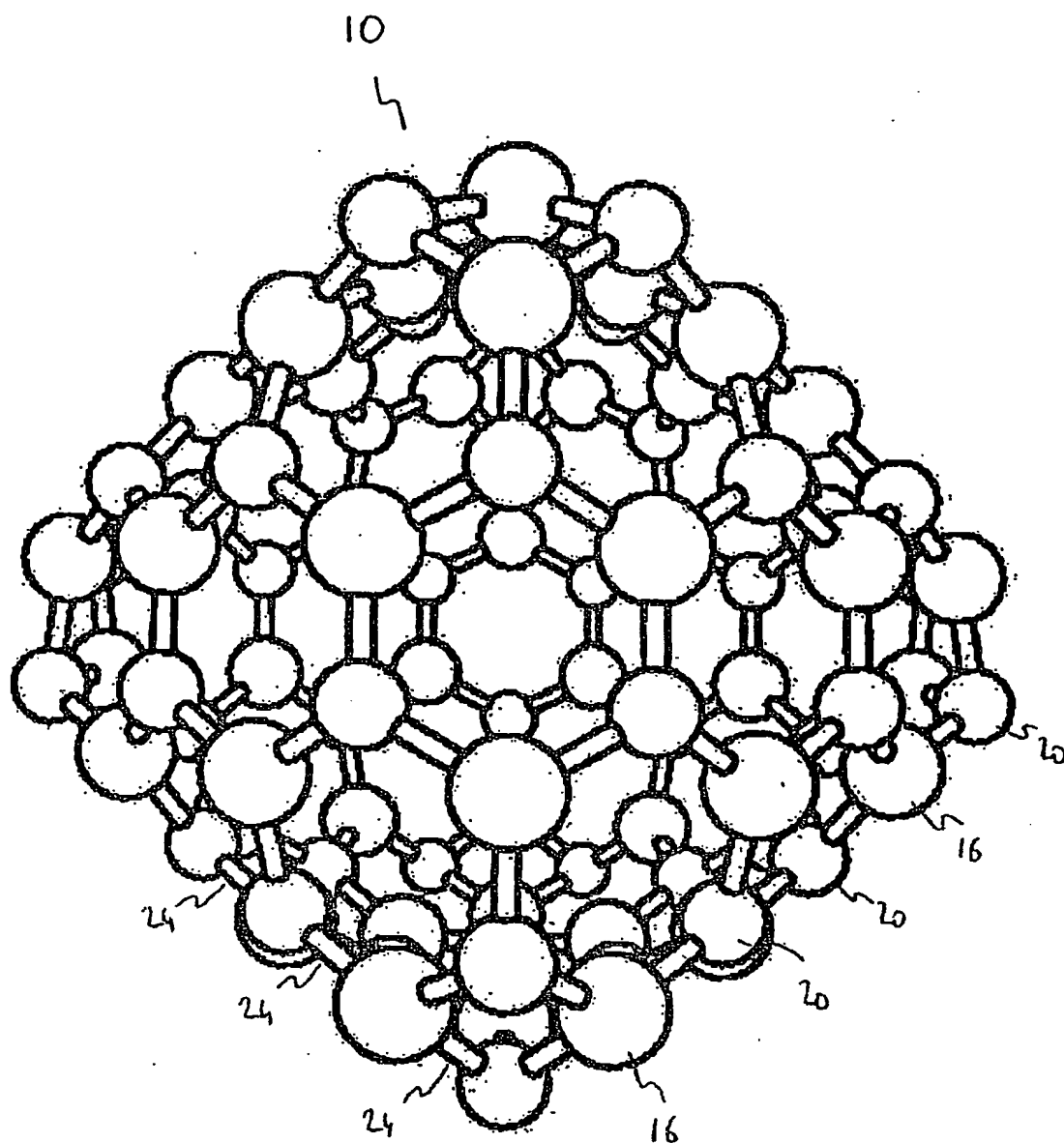


Figure 6

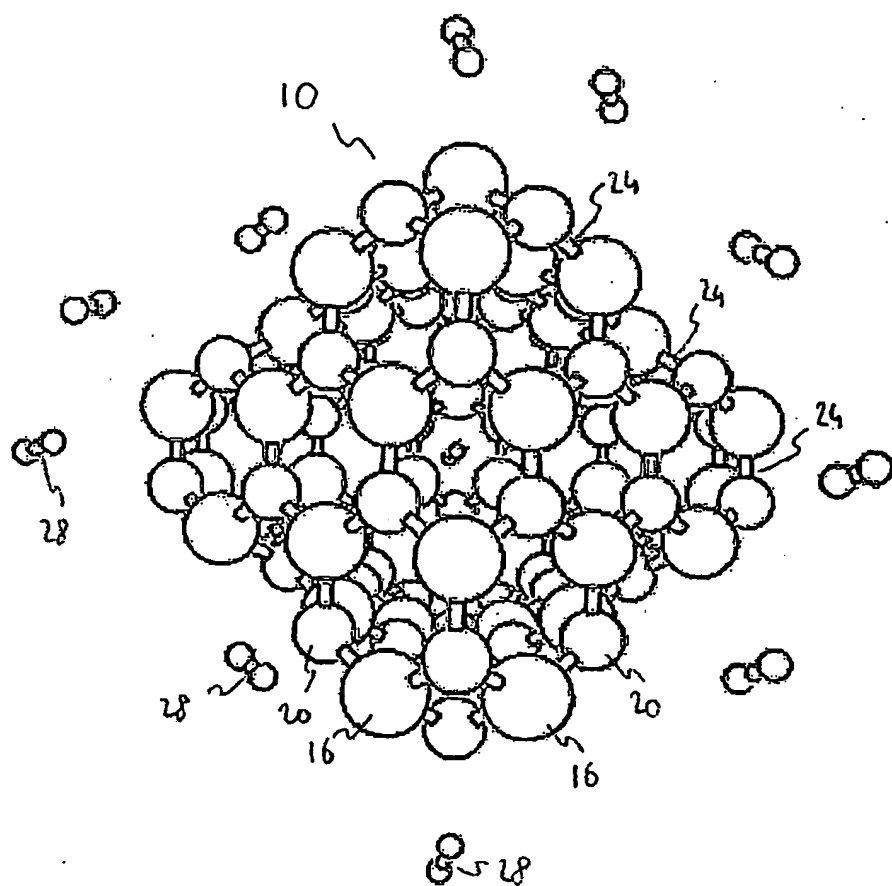


Figure 7

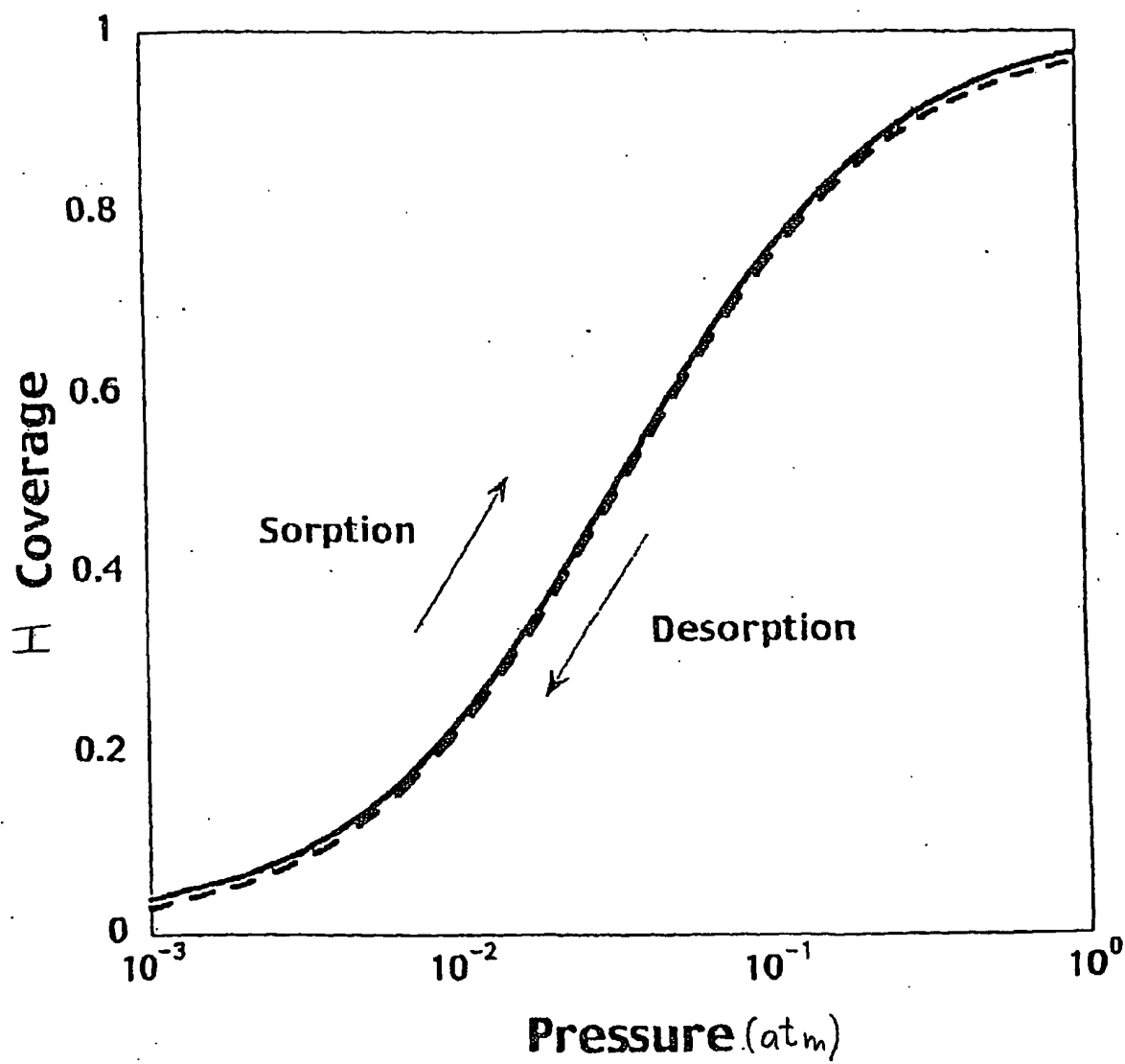


Figure 8

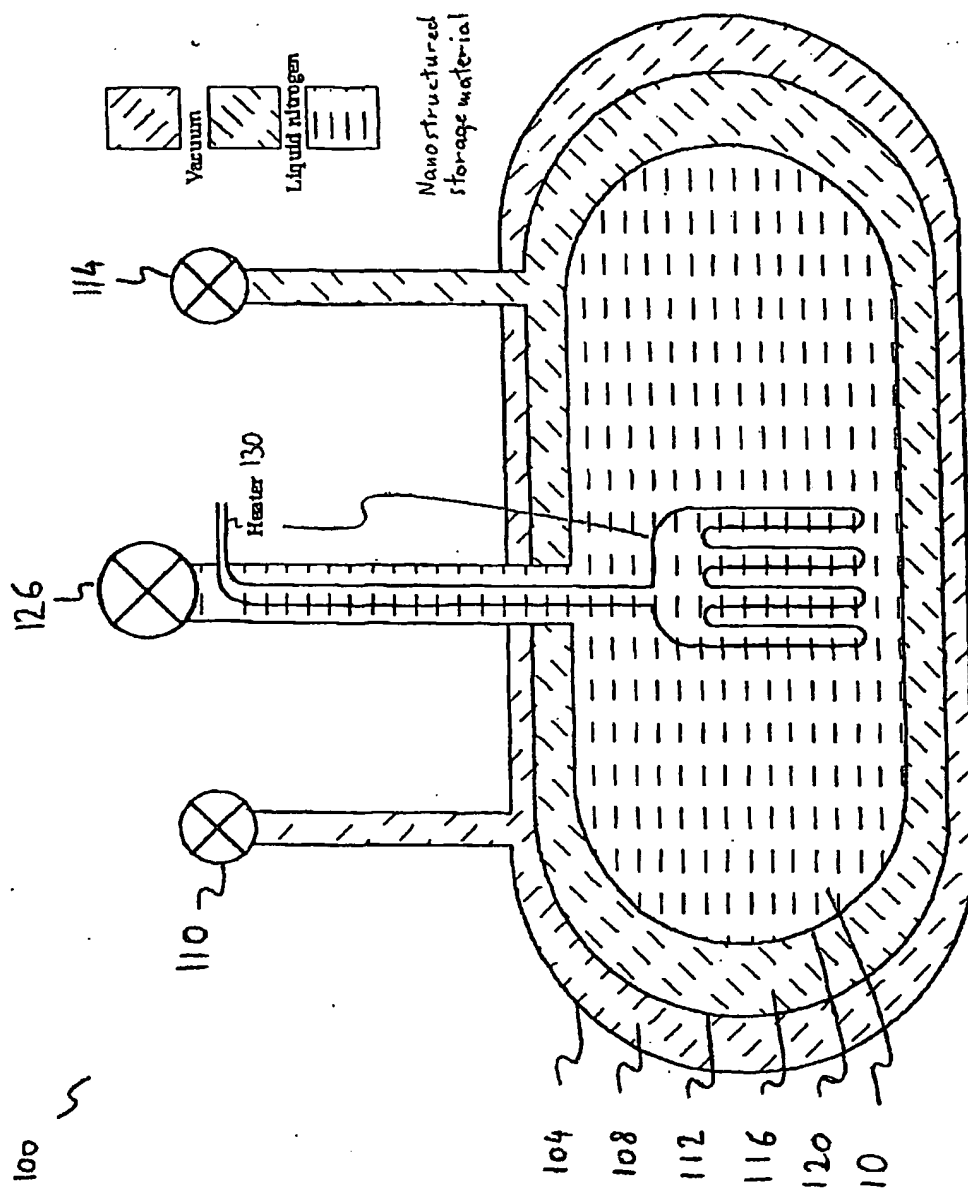


Figure 9

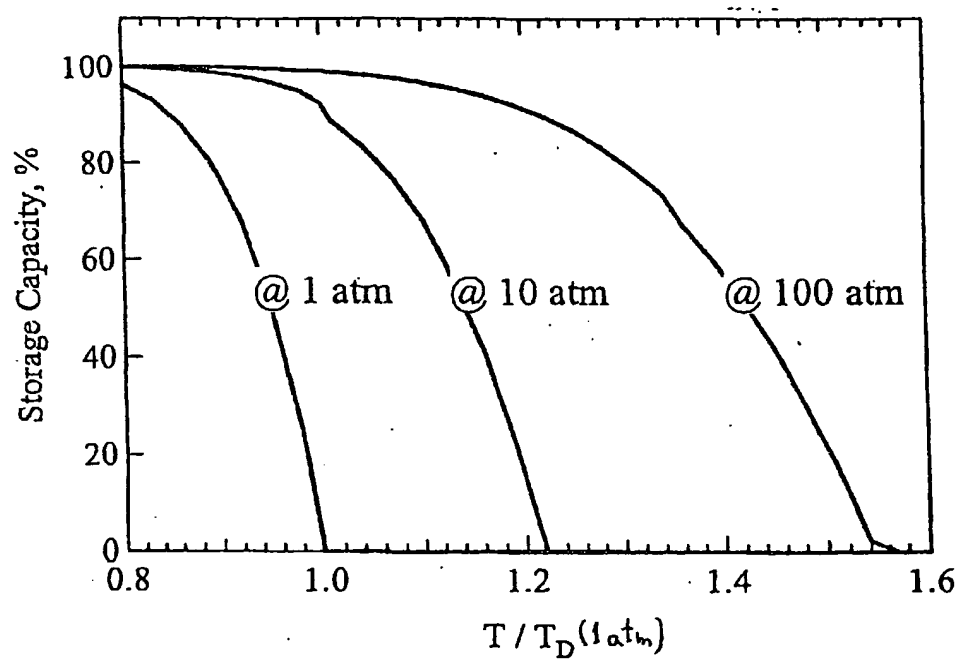


Figure 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/39695

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : F17C 11/00

US CL : 62/46.2

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 62/46.2, 45.1, 46.1, 440, 451

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,653,951 A (RODRIGUEZ et al.) 05 August 1997, Abstract; column 2, lines 14-17.	1-10
A	US 6,290,753 B1 (MAELAND et al.) 18 September 2001, entire document.	1-10
Y	US 6,231,980 B1 (COHEN et al.) 15 May 2001, Abstract.	4 and 5

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:		"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

09 FEBRUARY 2003

Date of mailing of the international search report

08 APR 2003

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